

Supporting Information for

Self-assembly of a neutral luminescent Au₁₂ cluster with D₂ symmetry

Qing-Fu Sun,^a Terence Kwok-Ming Lee,^b Pei-Zhou Li,^a Liao-Yuan Yao,^a Jing-Jing Huang,^a Jing Huang,^a Shu-Yan Yu,^{*a} Yi-Zhi Li,^c Eddie Chung-Chin Cheng^b and Vivian Wing-Wah Yam^{*b}

^a Laboratory for Self-Assembly Chemistry, Department of Chemistry, Renmin University of China, Beijing, 100872, China. Fax: (+8610) 62516614; Tel: (+8610) 62516614; E-mail: yusy@chem.ruc.edu.cn.

^b Centre for Carbon-Rich Molecular and Nano-Scale Metal-Based Materials Research, Department of Chemistry and HKU-CAS Joint Laboratory on New Materials, The University of Hong Kong, Pokfulam Road, Hong Kong, China. Fax: (+852) 28571586; Tel: (+852) 28592153; E-mail: wwyam@hku.hk.

^c State Key Laboratory of Coordination Chemistry, Coordination Chemistry Institute, Nanjing University, Nanjing, 200093, China.

*To whom correspondence should be addressed. E-Mail: yusy@chem.ruc.edu.cn (S.Y.Y.); wwyam@hku.hk (V.W.W.Y.).

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Figure S1. ¹H NMR of Au₁₂ in CDCl₃

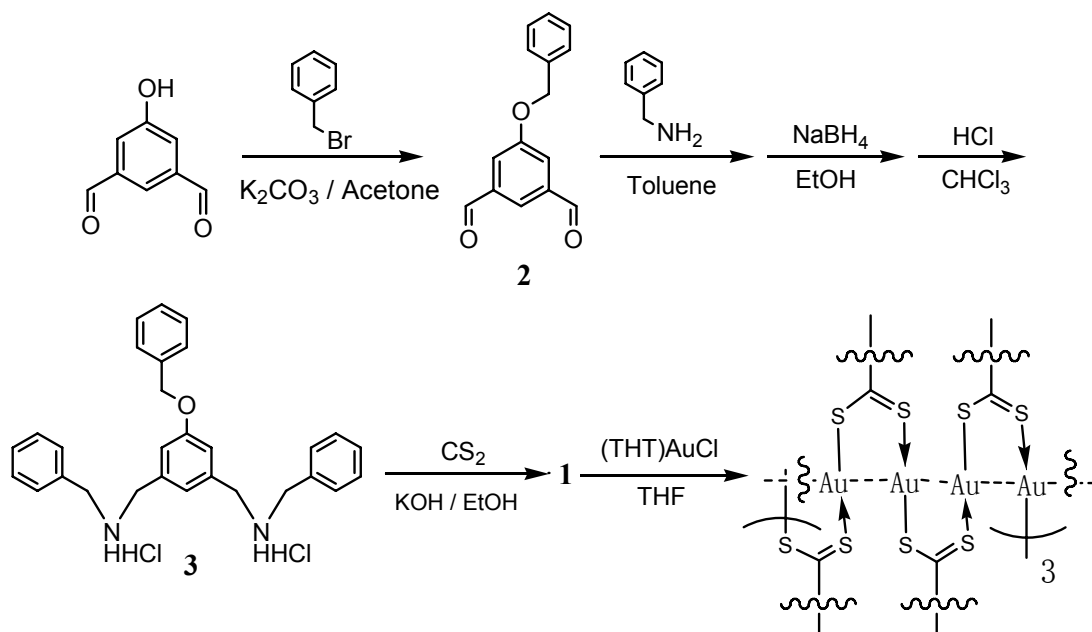
Figure S2. ¹H-¹H COSY of Au₁₂ in CDCl₃

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Table S1. Crystal Data and Details of the Structure Determination for Au₁₂

Text S1. Experimental Details.

The Au₁₂ cluster was synthesized as shown in Scheme S1:



Scheme S1. Synthetic route to the Au₁₂ cluster.

5-Hydroxyisophthalaldehyde was synthesized according to a literature method (1) in nearly quantitative yield. (¹H NMR, 400 MHz, CDCl₃: δ 10.03 (s, 2H, -Ar-CHO), 8.01 (s, 1H, -Ar-OH), 7.91 (s, 1H, Ar-H₂), 7.69 (s, 2H, -Ar-H_{4,6}). 5-hydroxyisophthalaldehyde was stirred with K₂CO₃ and benzyl bromide in acetone to give **2** (81%) (¹H NMR, 400 MHz, CDCl₃: δ 10.03 (s, 2H, -CHO), 7.96 (s, 1H, Ar-H), 7.72 (s, 2H, Ar-H), 7.46-7.34 (m, 5H, -CH₂-Ar-H), 5.28 (d, 2H, Ar-CH₂). The condensation reaction was carried out in a refluxing toluene solution of **2** and phenylmethanamine. The given Schiff base was instantly reduced by NaBH₄ in ethanol to afford the secondary amine, which was further purified by transforming to its HCl salt in chloroform and recrystallized in a mixture of chloroform and ethanol to give **3** as a white powder (65%). (¹H NMR, 400 MHz, DMSO-d₆: δ 9.84 (b, 4H, -NH₂Cl), 7.57-7.20 (m, 18H, -Ar-H), 5.14 (s, 2H, -O-CH₂-), 4.13-4.10 (m, 8H, -N-CH₂-)).

Due to the instability of the dithiocarbamate ligand, the self-assembly process was carried out in a one-pot reaction. A slight excess of CS₂ was added to a solution of **3** and KOH in ethanol, and the reaction was subjected to vigorous stirring for 30 minutes. This solution of ligand **1** was then immediately used for the self-assembly process after evaporation of the excess CS₂. Addition of (THT)AuCl (THT = tetrahydrothiophene) in dichloromethane to a solution of 0.5 mol equiv. of **1** in ethanol at room temperature resulted in the formation of a yellow precipitate. Evaporation of the reaction mixture followed by flash chromatography of the residue with chloroform as the eluent gave the titled product as a yellow solid in 90% yield. (Anal. Calcd for C₁₈₆H₁₆₈Au₁₂N₁₂O₆S₂₄ (5800.56): C, 38.51; H, 2.92; N, 2.90. Found: C, 38.21; H, 3.08; N, 2.98).

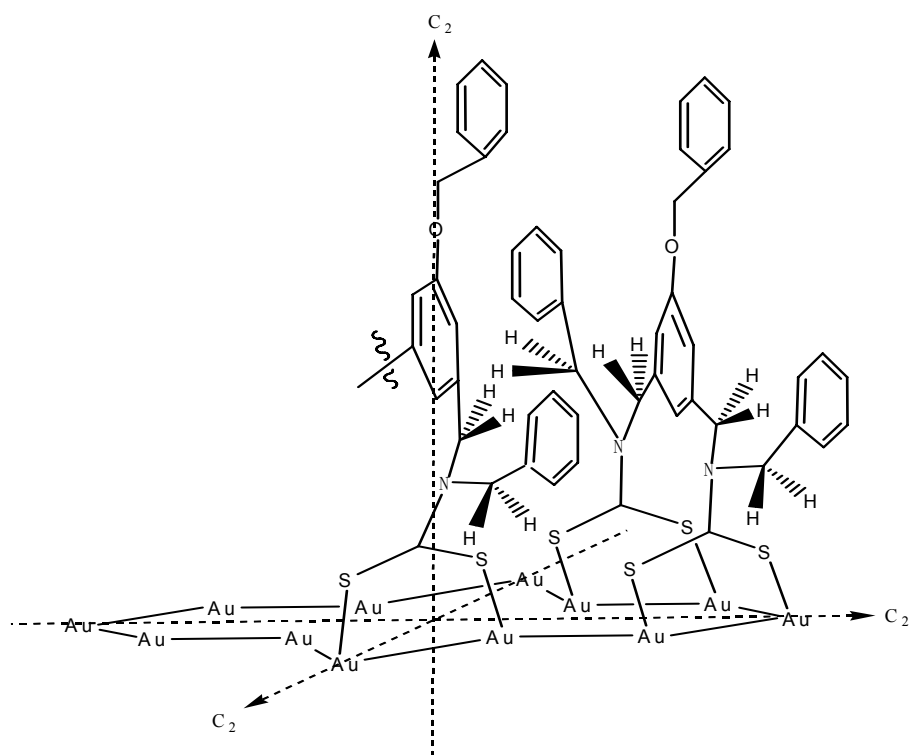
Text S2. X-Ray Method.

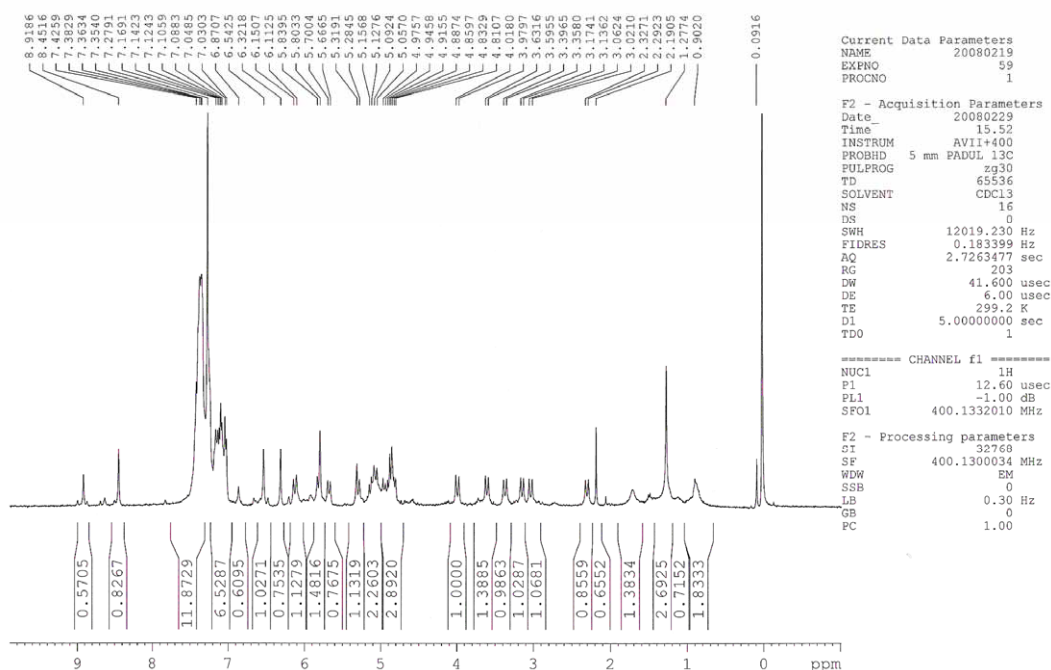
X-Ray diffraction measurements for the Au₁₂ were carried out at 291 K on a Bruker Smart Apex II CCD area detector equipped with a graphite monochromated MoK α radiation ($\lambda = 0.71073$ Å). The absorption correction was performed using SADABS. The structures were solved by direct method and refined employing full-matrix least-squares on F² by using SHELXTL (Bruker, 2000) program and expanded using Fourier techniques. All non-H atoms of the complexes were refined with anisotropic thermal parameters. The hydrogen atoms were included in calculated positions. Crystal data and details of the structure determination for Au₁₂ are summarized in Table S1.

Text S3. Photophysical Measurements and Instrumentation.

The electronic absorption spectra were recorded on a Hewlett–Packard 8452A diode array spectrophotometer. The solid-state photophysical measurements at 77 K were carried out with the solid sample loaded in a quartz tube inside a quartz-walled Dewar flask filled with liquid nitrogen and the steady-state emission spectra were recorded on a Spex Fluorolog-3 Model FL3–211 fluorescence spectrofluorometer. Luminescence lifetime measurements were performed using a conventional laser system. The excitation source was the 355 nm output (third harmonic) of a Spectra-Physics Quanta-Ray Q-switched GCR-150-10 pulsed Nd-YAG laser. The luminescence decay signals from a Hamamatsu R928 PMT were converted to voltage changes by connecting to a 50 Ω load resistor and were then recorded on a Tektronix Model TDS-620A digital oscilloscope. The lifetime τ was determined by a single exponential fitting of the luminescence decay trace with the relationship $I = I_0 \exp(-t/\tau)$, where I and I_0 are the luminescence intensity at time = t and 0, respectively.

Figure S1. ^1H NMR of Au_{12} in CDCl_3





^1H NMR, 400 MHz, CDCl_3 : δ 8.92 (s, 2H, -O-Ar-H), 8.45 (s, 4H, -O-Ar-H), 7.43-7.03 (m, 80H, - CH_2 -Ar-H), 6.87 (s, 2H, -O-Ar-H), 6.54 (s, 4H, -O-Ar-H), 6.32 (s, 4H, -O-Ar-H), 6.15 (d, 4H, -Ar- CH_2 -N-), 5.83 (d, 4H, -Ar- CH_2 -N-), 5.80 (s, 2H, -O-Ar-H), 5.70 (d, 4H, -Ar- CH_2 -N-), 5.31 (d, 4H, -N- CH_2 -Ar), 5.16 (d, 4H, -N- CH_2 -Ar), 4.85 (d, 4H, -N- CH_2 -Ar), 4.98-4.81 (m, 12H, -O- CH_2 -Ar), 4.02 (d, 4H, -Ar- CH_2 -N-), 3.63 (d, 4H, -Ar- CH_2 -N-), 3.40 (d, 4H, -N- CH_2 -Ar), 3.17 (d, 4H, -N- CH_2 -Ar), 3.06 (d, 4H, -N- CH_2 -Ar), 2.32 (d, 4H, -Ar- CH_2 -N-)

Figure S2. ^1H - ^1H COSY of Au_{12} in CDCl_3

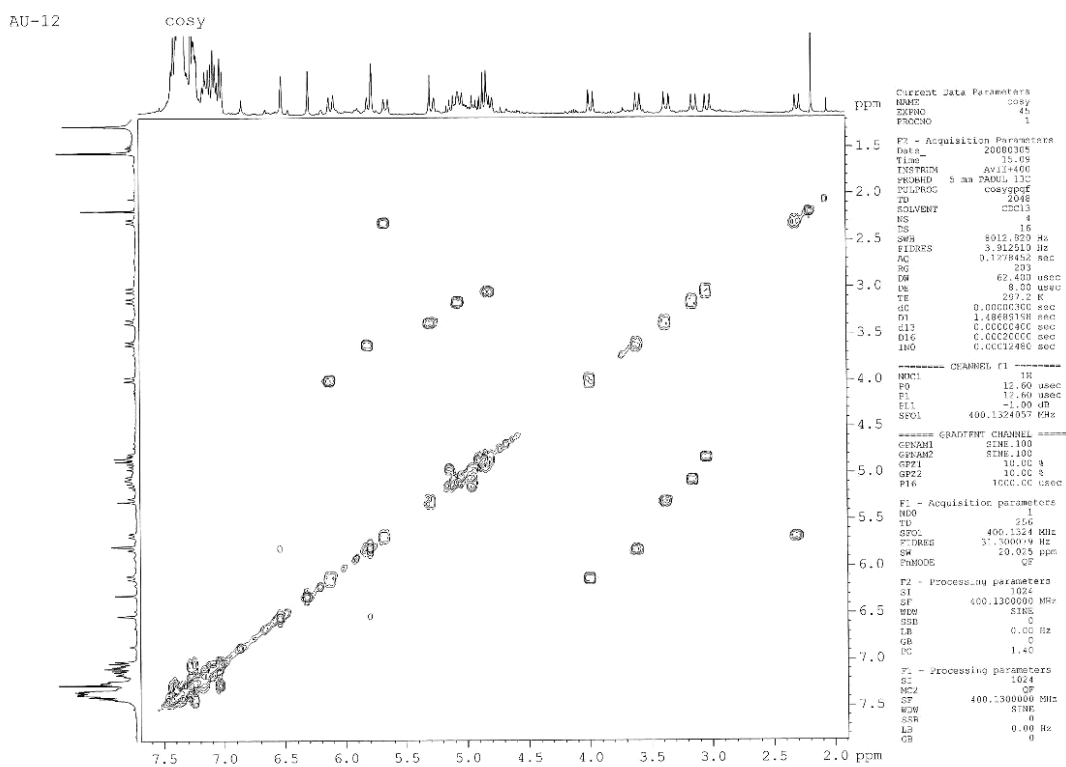
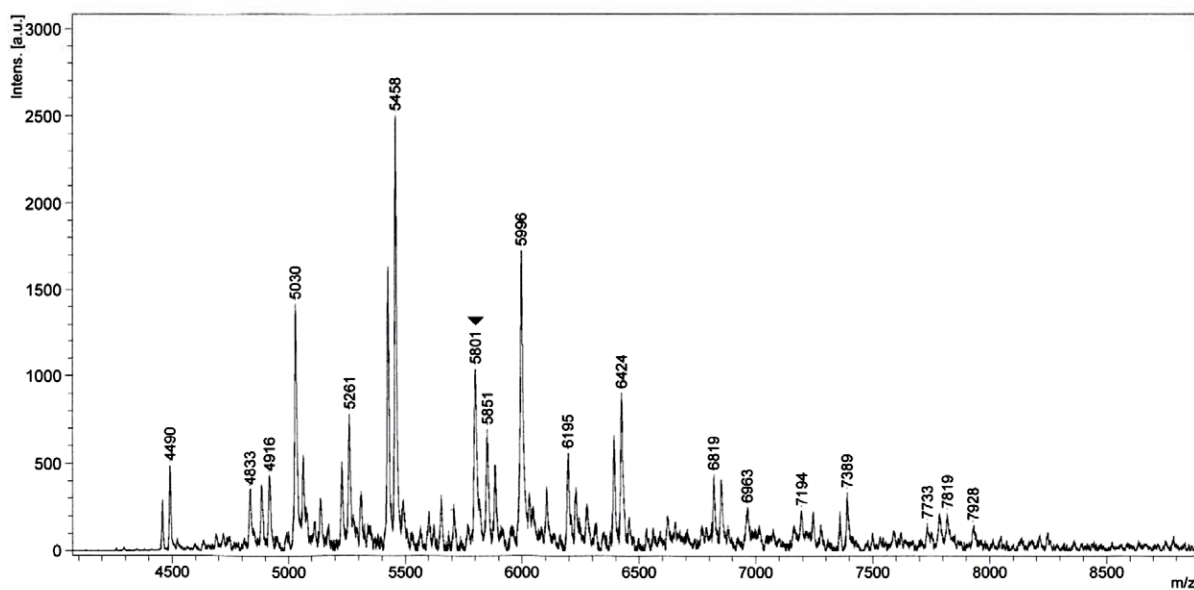


Figure S3. MALDI-TOF-MS of Au₁₂

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MALDI-TOF,DHB,2007,09,13



Linear Model: m/z 5801 [Au₁₂L₆]; 5996 [Au₁₃L₆]; 6195 [Au₁₄L₆]; 6393 [Au₁₅L₆]. Some of the remaining fragment peaks were tentatively assigned: m/z 5030 [Au₈L₆ + H₂O]; 5229 [Au₉L₆ + H₂O]; 5261 [Au₉L₆ + S + H₂O]; 5426 [Au₁₀L₆ + H₂O]; 5458 [Au₁₀L₆ + S + H₂O]; 5851 [Au₁₂L₆ + S + H₂O]; 5884 [Au₁₂L₆ + 2S + H₂O]; 6424 [Au₁₅L₆ + S]; 6819 [Au₁₇L₆ + S].

Table S1. Crystal Data and Details of the Structure Determination for Au₁₂

Formula	C ₁₈₆ H ₁₆₈ Au ₁₂ N ₁₂ O ₆ S ₂₄ , 3CHCl ₃ , 7H ₂ O
Formula Weight	6284.58
Crystal System	Triclinic
Space group	P-1 (No. 2)
Unit cell dimensions	a = 18.3910(9) Å, alpha=84.629(2) ° b = 21.5894(11) Å, beta=82.1110(18) ° c = 28.2586(14) Å, gamma=88.706(2) °
Volume	11064.6(10) Å ³
Z	2
Density (calculated)	1.886 g cm ⁻³
F(000)	5984
Crystal Size	0.20 x 0.18 x 0.15 mm ³
Temperature	291(2) K
Theta range for data collection	0.95-26.0
Index ranges	-20 ≤ h ≤ 22, -22 ≤ k ≤ 26, -34 ≤ l ≤ 27
Reflections collected	119200
Independent reflections	42914 [R(int) = 0.0386]
Completeness to theta = 26.0°	98.6%
Absorption correction	Semi-empirical from equivalents
Refinement method	Full-matrix least-squares on F ₂
Data / restraints / parameters	42914 / 0 / 2395
Goodness-of-fit on F ²	1.039
Final R indices [I > 2sigma(I)]	R1 = 0.0487, wR2 = 0.1069
R indices (all data)	R1 = 0.0693, wR2 = 0.1115
Largest diff. peak and hole	0.736 and -1.563 e Å ⁻³

(1) A. Star, Y. Liu, K. Grant, L. Ridvan, J. F. Stoddart, D. W. Steurman, M. R. Diehl, A. Boukai, and J. R. Heath.
Macromolecules, 2003, **36**, 553-560.